Supporting Information

Highly Selective and Efficient Extraction of Lignin in Kraft Pulp by Aqueous Ionic Liquids for Enhanced Bleaching Properties

Zhiqiang Pang*, Jiachuan Chen, Cuihua Dong, Guihua Yang

Experimental Section

Materials

Unbleached *Eucalyptus Grandis* kraft pulp was cooked in a 15 L batch cylindrical rotatory digester. The operating conditions for kraft pulping were as follows: active alkali charge of 18% (measured by Na_2O), liquor/wood ratio of 4:1, maximum temperature of 165 °C, time to maximum temperature of 90 min, and time at maximum temperature of 120 min. The cooked fibers were washed thoroughly with tapped water and then screened with 0.30 mm slotted plate. The pulps were kept in a vacuum oven at 50 °C for 48 h before ionic liquids (ILs) treatment for water removal. All other chemical reagents were purchased from commercial sources in China. 1-butyl-3-methylimidazolium chloride (BmimCl) was synthesized as described by Huddleston et al., whereas 1-allyl-3-methylimidazolium chloride (AmimCl) was synthesized according to the general procedure described by Zhang et al.[1] All IL samples were dried using an oil pump vacuum at 80 °C for several days to remove residual water and solvent traces.

Pulp Pretreatment by Aqueous ILs

The vacuum-dried pulp samples (15 g, oven dry weight) were homogeneously mixed with ionic liquid and water. Afterwards, the slurries were decanted into a 500 ml dried flask equipped with a mechanical stirrer under an inert nitrogen atmosphere. The temperature of the pretreatment process was controlled by oil bath. Pretreatment termination was accomplished by pouring water (100 ml) into the slurry, which were then washed thoroughly to remove the residual ionic liquids.

Bleaching

The pulps were put into a poly-plastic bag and preheated in a temperature controlled water bath, then mixed with bleaching liquor manually, sealed and put back into a temperature controlled water bath. The bags were taken out and mixed once manually at each time interval of 15 min during whole bleaching duration. The

conditions of chlorine dioxide bleaching (D) stage are ClO_2 dosage of 0.8wt%, 70 °C, 120 min, ends pH of 3.8. The conditions of Chelation bleaching (Q) stage are as follows diethylene triamine pentacetic acid (DTPA) dosage of 0.25wt%, 70 °C, 40 min, and the final pH of 3.5. The conditions of Hydrogen Peroxide bleaching (P) are as follows: H_2O_2 dosage of 2.5%, NaOH dosage of 2.0%, Na_2SiO_3 dosage of 3.0%, $MgSO_4$ dosage of 0.05%, 70 °C, 120 min. The effluent of bleaching were gathered at end of bleaching stages for further analysis and then pulps were thoroughly washed with tapped water at ends of bleaching stages.

Determination of Effluent Properties in Bleaching Stages

COD, BOD and AOX of DQP bleaching effluent are determined on basis of unbleached pulp. Determination of COD and BOD is according to ISO 15705-2002 and ISO 5815-1-2003, respectively. And determination of AOX is according to SCAN-W9:89.

Pulp Characterization

Brightness of pulp is measured according to TAPPI standard T452 om-08, and the yield of bleaching is ration of oven mass of pulp before and after bleaching.

Fiber width was determined using a fiber quality analyzer (FQA; Canada OpTest Company, model LDA02).

The viscosity of the pulps was measured according to the TAPPI standard T230 om-08 method.

The specific surface area of pulp was determined using N_2-BET adsorption method with Specific surface analyzer (V-Sorb2800P, Gold APP, China)

The XRD curve of samples were scanned on a D8 Advance X-ray diffractometer (Bruke, Germany), with a Co radiation source at 40 kW and 35 mA, a scan speed of 0.18 min^{-1}, and a step size of 0.018°. The crystallinity index was determined using the method described by Segal et al. [2]

The FTIR spectra of lignin samples were recorded using an FTIR technique (IRPretige-21, Shimadzu, Japan) using KBr-pellet method. The spectrum was scanned in the range 400 to 4000 cm^{-1} wave numbers.

Determination of Lignin Contents

Lignin content in pulps, including Klason lignin and acid-soluble lignin, were determined according to TAPPI Test and Useful Methods (T222 om-8 and UM 250,

respectively).

Isolation and Characterization of Lignin in Pulp

The residual lignin in pulps were isolated and purified by the enzymatic-mild acidic hydrolysis method.[3] The content of hydroxyl group in lignin was measured by the quantitative ^{31}P-NMR Spectroscopic Analysis, which carried out on a Bruker Avance II400 spectrometer. Oven-dried lignin samples (40 mg) were dissolved in pyridine/chloroform (1.6:1, V/V) by stirring continuously for several hours. N-hydroxyl naphthalimide and chromium acetylacetonate were used as the internal standard and the relaxation reagent, respectively. Phosphitylation of hydroxyl groups were achieved using 2-chlorl-4, 4, 5, 5-tetramethyl-1, 3, 2-dioxa-phospholane.

The acetylation of lignin was achieved by dissolution in pyridine/acetic acid (1:1, v/v) for 24 h at room temperature, then drop wise added into excess methanol/water (1:1, v/v) solution and placed in refrigerator overnight. The acetylated lignin was collected by centrifugation. The acetylated lignin samples were dissolved in tetrahydrofuran with concentration of 1.0 mg/mL. The conditions of GPC analysis are as follows: Shim-pack GPC-803 column, 300 mm l×8 mm ID gel column, tetrahydrofuran as mobile phase with volume flow rate of 0.5 ml/min, column temperature of 35 °C, injection volume of 15 μL, polystyrene with molecular weight 1930, 2900 and 31400 as standards, and ultra-violent detector at 280 nm.

Coverage of Lignin on Fiber Surface

Lignin coverage on fiber surface was determined using the O/C peak ration in XPS spectra, which were obtained with a Perkin Elmer PHI 5300 ESCA instrument equipped with a monochromatic Al Kα X-ray source, and vacuum degree is 1.3×10^{-5} Pa, resolution is 0.80 eV, counting rate is 80000 cps. The hand sheets of pulps were obtained using Buchner funnel, and 30%, 50%, 70%, 90%, 95% and 100% ethanol solutions were used to achieve gradient dewatering of the samples. The empirical composition of polysaccharide was represented by C_6O_5, and the empirical formula for the lignin component was represented by $C_{9.92}O_{3.32}$, and percent coverage of lignin on fiber surface was determined as Eq. S(1).

$$\Phi_{\text{lignin}}=[(N_O/N_C)_{\text{pulp sample}}-(N_O/N_C)_{\text{polysaccharide}}]/[(N_O/N_C)_{\text{lignin}}-(N_O/N_C)_{\text{polysaccharide}}] \quad \text{S(1)}$$

Tables and Figures

Table S1. DQP bleaching properties of pulps pretreat by AmimCl.

Water content, %	Lignin content, %	Viscosity, mL/g	Brightness, %ISO	Yield, %	COD, mg/g pulp	BOD, mg/g pulp	AOX, mg/g pulp
0	2.28	766.1	83.0	86.2	64.9	14.3	0.38
3	2.24	765.0	83.2	86.3	65.2	14.4	0.37
6	2.38	768.6	82.1	86.6	66.5	14.5	0.40
9	2.62	771.5	80.8	86.8	67.3	14.6	0.43
12	2.82	774.8	79.0	87.0	67.9	14.7	0.48
15	2.98	775.2	78.5	87.1	68.1	14.7	0.51
Control sample							
		775.6	78.3	87.2	68.2	14.8	0.53

Table S2. The bleaching properties with decreasing bleaching chemicals (3.0 mL BmimCl/g pulp with water content of 3% at 70 °C for 30 min).

Decrease of bleaching chemicals, %	Viscosity, mL/g	Brightness, %ISO	Yield, %	COD, mg/g pulp	BOD, mg/g pulp	AOX, mg/g pulp
0	767.5	82.7	86.6	65.8	14.5	0.39
15	782.6	80.6	87.5	59.2	13.1	0.35
20	791.3	79.2	87.9	56.4	12.4	0.33
25	800.6	78.4	88.4	52.1	12.0	0.31
30	816.5	77.2	89.3	50.4	11.4	0.30
Control sample						
	775.6	78.3	87.2	68.2	14.8	0.53

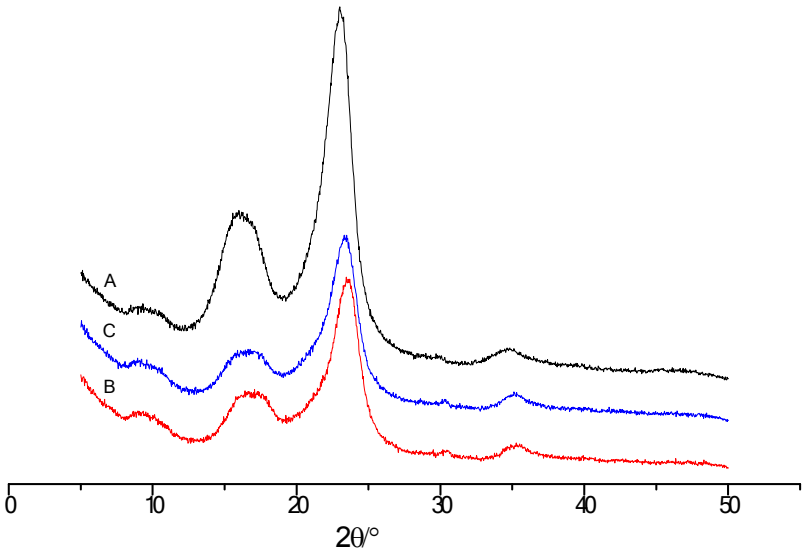
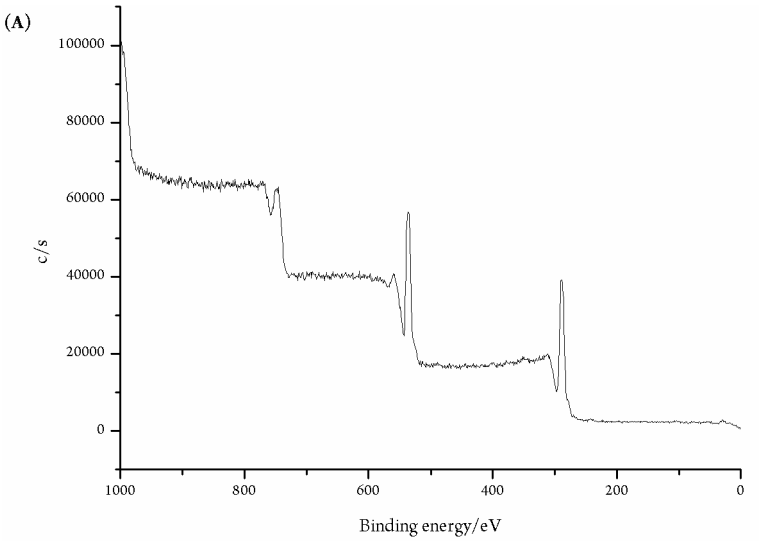


Figure S1. Fiber XRD Chart of KP before and after aqueous ILs pretreatment (A= the control sample; B= the sample after BmimCl treatment; C=the sample after AmimCl treatment).



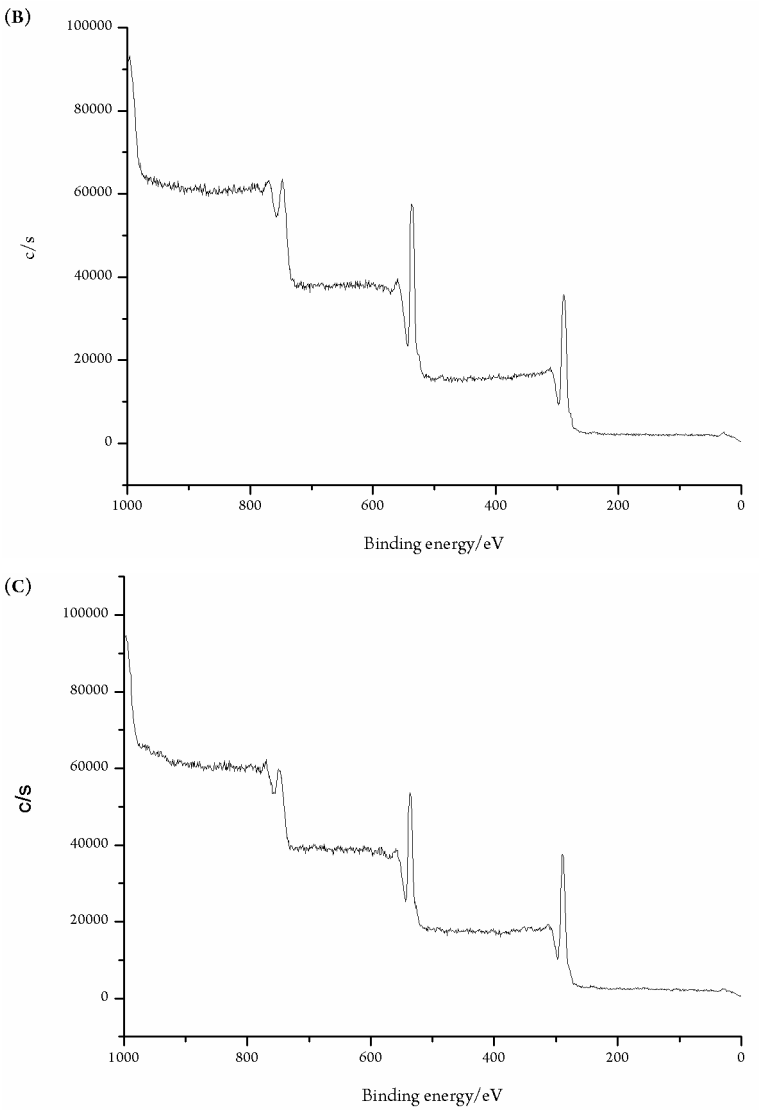


Figure S2. XPS spectra of the pulps (A= the control sample; B= sample after BmimCl treatment; C= sample after AmimCl treatment).

References

1. J. G. Huddleston, A. E. Visser, W.M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, *Green Chem.* 2001, **3**, 156.
2. H. Zhang, J. Wu, J. Zhang, J. S. He, *Macromolecules* 2005, **38**, 8272.
3. D. S. Argyropoulos, Y. Sun, E. Palus, *J. Pulp Pap. Sci.* 2002, **28**, 50.